MECHANISM AND INTERMEDIATES OF METHANOL SYNTHESIS OVER THE Cu/ZnO CATALYST IN THE PRESENCE OF WATER AND CARBON DIOXIDE

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INTRODUCTION

Since Sabatier's first experiments on heterogeneously catalyzed methanol decomposition (1), many studies have been devoted to the mechanism of both the decomposition and the synthesis of methanol, and surface intermediates such as formyl (2,3), formate (4-6), and methoxide (4,5) have been identified by IR spectroscopy and chemical trapping techniques. In a previously reported (7) study from our laboratory, it was found that the methanol synthesis rate over Cu/ZnO catalyst is greatly enhanced by small additions of water to the synthesis gas while large additions of water resulted in a decrease in synthesis rate. Comparison of the water effect with that of CO_2 on the synthesis rate (8) showed that water behaved as a more effective promoter at low concentrations and a more severe retardant at higher concentrations than did equimolar carbon dioxide at the same experimental conditions. Further, injection of a 65/35 mole % mixture of $H_2^{18}O/H_2^{16}O$ to synthesis gas resulted in ^{18}O incorporation, the % ^{18}O in CH_3OH, CO and CO_2 in the exit stream being 3.41, 0.60 and 3.56, respectively. These results indicated that H_2O and/or CO_2 participate in methanol synthesis as reactants. D_2O addition to the synthesis gas was employed to further determine the kinetic and mechanistic role of water, and it was observed that a significant portion of the synthesized methanol occurred as CH_2DOH. No CHD_2OH or CD_3OH was detected, and these results indicated that water was involved in the formation of an intermediate with one single hydrogen atom. This observation was further supported by the promotion of isotopic scrambling between $^{12}C^{18}O$ and $^{13}C^{16}O$ by water preadsorption on the catalysts.

Chemical trapping experiments were also used (7) in identifying reactive intermediates involved in methanol synthesis. When diethylamine was continuously injected along with the synthesis gas, methylated tertiary amine was selectively obtained by the reaction:

$$(C_2H_5)_2NH + CO + 2H_2 \longrightarrow (C_2H_5)_2NCH_3 + H_2O . \qquad 1)$$
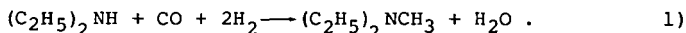
At 215°C, H_2:CO = 70:30, 75 atm and a molar feed rate of diethylamine = 14.5 mmol/2.45 g cat/hr, the yield of methyldiethylamine was 11.2 mmol/2.45 g cat/hr and 97% of the water formed during methylation of diethylamine was converted to carbon dioxide by the water gas shift reaction. Amine addition, however, was not found to affect the water gas shift reaction. The intermediate trapped by amine behaved chemically as formyl, formaldehyde or hydroxycarbene. The evidence for an aldehydic intermediate was further corroborated by utilizing it for aldol addition with propanaldehyde followed by hydrogenation to give 2-methyl-1-propanol. Although both the above trapping reactions allowed a fairly complete mechanism to be formulated, it was still deemed necessary to address some alternative trapping and side reactions, particularly those of amines with surface formates.

It is known that (9) amines react with carboxylic acids to give acid amides, which could be hydrogenated to the corresponding amines (10). In order to determine whether the added diethylamine reacted more rapidly with surface formyl or formate, the hydrogenation of N,N-diethylformamide, a suspected intermediate of the reaction of surface formate with diethylamine, was studied. It is reported herein that non-dissociative hydrogenation of N,N-diethylformamide occurs at a lower rate than the addition of synthesis gas to diethylamine 1), indicating that the amine trapped the aldehydic and not the formate intermediate under the synthesis conditions.
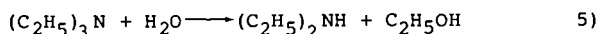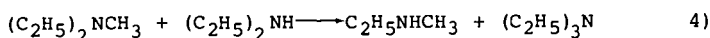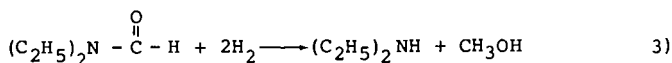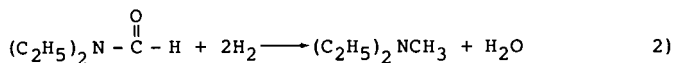
EXPERIMENTAL

The Cu/ZnO = 30/70 mol % catalysts were coprecipitated from nitrate solution by Na_2CO_3, calcined, pelletized, and reduced with 2% hydrogen in nitrogen, according to a procedure previously described in detail (11,12). A schematic of the catalytic reactor system has been presented (11), but a high pressure unit for pumping liquids into the synthesis gas stream at the reactor pressure of 75 atm has been added at the top of the reactor preheater section. The exit gas was reduced to atmospheric pressure and was sampled by an on-line Hewlett-Packard 5730A GC, coupled with a Model 3388A integrator/controller.

RESULTS AND DISCUSSION

The results of N,N-diethylformamide hydrogenation at 215°C and 75 atm are given in Table I. When the flow rate of N,N-diethylform-amide was 10.8 mmol/2.45 g cat/hr, 62% of it was converted to diethyl-methylamine and the remaining 38% was distributed among other products. When the flow rate of N,N-diethylformamide and hydrogen was doubled and tripled at 215°C and 75 atm, the yields of diethylamine and methanol increased while the yield of all other products decreased (Table I).

As indicated in Table I, the N,N-diethylformamide was completely converted to diethylmethylamine (Eqn. 2), methanol (Eqn. 3), diethyl-amine (Eqn. 3), methylethylamine (Eqn. 4), triethylamine (Eqn. 4), and ethanol (Eqn. 5).

$$(C_2H_5)_2N - \overset{\overset{\text{O}}{\|}}{C} - H \ + \ 2H_2 \longrightarrow (C_2H_5)_2NCH_3 \ + \ H_2O \qquad\qquad 2)$$

$$(C_2H_5)_2N - \overset{\overset{\text{O}}{\|}}{C} - H \ + \ 2H_2 \longrightarrow (C_2H_5)_2NH \ + \ CH_3OH \qquad\qquad 3)$$

$$(C_2H_5)_2NCH_3 \ + \ (C_2H_5)_2NH \longrightarrow C_2H_5NHCH_3 \ + \ (C_2H_5)_3N \qquad\qquad 4)$$

$$(C_2H_5)_3N \ + \ H_2O \longrightarrow (C_2H_5)_2NH \ + \ C_2H_5OH \qquad\qquad 5)$$

The reactions given by Eqn. 4) and 5) were formulated by CH_3, C_2H_5 and H_2O balancing. Hence, a part of diethylmethylamine and
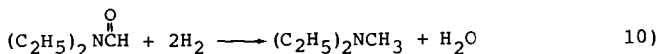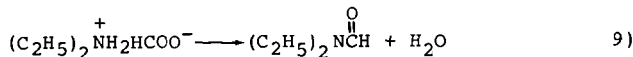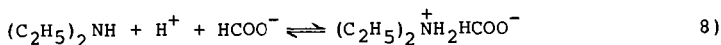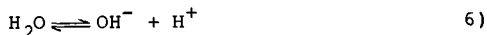
TABLE I

HYDROGENATION OF N,N-DIETHYLFORMAMIDE (NNDEF) AT 215°C, 75 atm OVER 2.45 g OF Cu/ZnO (30/70) CATALYST

Flow Rate of Substrate	Flow Rate of Hydrogen		H_2O	CH_3OH	C_2H_5OH	MEA	DEA	DEMA	TEA	NNDEF	CO	CO_2
Experiment (A)												
20 µl/min of NNDEF	10.5 ℓ (STP)/hr	mmol/hr In	--	--	--	--	--	--	--	10.8	--	--
		mmol/hr Out	7.6	2.9	0.5	1.4	1.9	6.7	0.9	<0.02	<0.02	<0.02
		Exit gas composition[a] (mol %)	34.70	13.24	2.28	6.39	8.68	30.59	4.11	<0.01	<0.01	<0.01
Experiment (B)												
40 µl/min of NNDEF	21.0 ℓ (STP)/hr	mmol/hr In	--	--	--	--	--	--	--	21.6	--	--
		mmol/hr Out	13.0	7.6	0.7	1.7	6.2	12.6	1.0	<0.02	<0.02	<0.02
		Exit gas composition[a] (mol %)	30.37	17.76	1.64	3.97	14.49	29.44	2.34	<0.01	<0.01	<0.01
Experiment (C)												
60 µl/min of NNDEF	31.5 ℓ (STP)/hr	mmol/hr In	--	--	--	--	--	--	--	32.4	--	--
		mmol/hr Out	19.1	13.0	0.8	2.0	11.0	18.3	1.1	<0.02	<0.02	<0.02
		Exit gas composition[a] (mol %)	29.25	19.91	1.23	3.06	16.85	28.02	1.68	<0.01	<0.01	<0.01

[a] Exit gas composition excluding hydrogen.

MEA = methylethylamine DEMA = diethylmethylamine
DEA = diethylamine TEA = triethylamine

diethylamine produced by reactions 2) and 3) was consumed by reactions 4) and 5) to produce ethylmethylamine, triethylamine and ethanol. In Figure 1, the amount of diethylmethylamine produced by reaction 2), diethylamine produced by reaction 3), methanol and water are plotted as a function of the reciprocal flow rate of hydrogen (flow rate N,N-diethylformamide = 0.025 x flow rate hydrogen). When these curves are extrapolated to infinite flow rate of hydrogen, the amounts of diethylmethylamine, diethylamine, methanol and water were 20%, 30%, 30% and 20%, respectively. This flow rate dependence study shows that there are two kinds of reactions occurring on the catalyst surface during the hydrogenation of N,N-diethylformamide: one giving rise to diethylmethylamine, and the other giving rise to diethylamine and methanol. Diethylmethylamine could be synthesized via two routes: one as in Eqn. 2) and the other by the condensation of diethylamine and methanol, produced by Eqn. 3). The results in Figure 1 indicate that the maximum amount of diethylmethylamine formed by direct hydrogenation (Eqn. 2)) was 40%.

In the following paragraphs the results of the hydrogenation of N,N-diethylformamide will be compared to the results of the methylation of diethylamine by synthesis gas (discussed in the Introduction section). This comparison is done to determine whether N,N-diethylformamide is an intermediate in methyldiethylamine synthesis from synthesis gas and diethylamine. Over Cu/ZnO catalyst, 14.5 mmol/2.45 g cat/hr of diethylamine reacted with synthesis gas to produce 11.2 mmol/2.45 g cat/hr of methyldiethylamine. When 10.8 mmol/2.45 g cat/hr of N,N-diethylformamide, approximately equal to the methyldiethylamine produced, was hydrogenated under conditions similar to methyldiethylamine synthesis, the conversion to methyldiethylamine was 62%. A comparison of these two experiments indicated that the rate of hydrogenation of N,N-diethylformamide to methyldiethylamine was lower than the rate of production of methyldiethylamine from synthesis gas and diethylamine. Hence, the synthesis gas and diethylamine reaction does not proceed exclusively via a N,N-diethylformamide intermediate. However, the participation of this intermediate to a lesser extent cannot be ruled out. The following path is suggested for the synthesis of methyldiethylamine from synthesis gas and diethylamine, which proceeds via a N,N-diethylformamide intermediate.

$$H_2O \rightleftharpoons OH^- + H^+ \qquad\qquad 6)$$

$$CO + OH^- \rightleftharpoons HCOO^- \qquad\qquad 7)$$

$$(C_2H_5)_2NH + H^+ + HCOO^- \rightleftharpoons (C_2H_5)_2\overset{+}{N}H_2HCOO^- \qquad 8)$$

$$(C_2H_5)_2\overset{+}{N}H_2HCOO^- \longrightarrow (C_2H_5)_2\overset{O}{\overset{\|}{N}}CH + H_2O \qquad 9)$$

$$(C_2H_5)_2\overset{O}{\overset{\|}{N}}CH + 2H_2 \longrightarrow (C_2H_5)_2NCH_3 + H_2O \qquad 10)$$

According to this scheme, the surface formate produced by the interaction of CO and surface hydroxyls will react with diethylamine (Eqn 8)) to form an amine salt (9). Upon heating, the amine salt will be converted to N,N-diethylformamide (9), and upon hydrogenation methyldiethylamine and water are produced (10). The flow rate

dependence study established that there are two basic pathways for
the hydrogenation of N,N-diethylformamide. One gives rise to metha-
nol and diethylamine (Eqn. 3)) and the other gives rise to the direct
hydrogenation product, methyldiethylamine (Eqn. 2)). At zero contact
time, the contribution of the latter path is 40%. At other conditions,
e.g. when 10.8 mmol/2.45 g cat/hr of N,N-diethylformamide was hydro-
genated with 10.5 ℓ(STP)/2.45 g cat/hr of hydrogen (Table I(A)), only
50% of the methyldiethylamine would be produced by reaction 2). The
remaining 50% was produced by the secondary reaction in which diethyl-
amine and methanol would undergo condensation probably via a formalde-
hyde intermediate.

If all the diethylamine injected (14.5 mmol/2.45 g cat/hr) during
the methylation of diethylamine with synthesis gas was converted to
N,N-diethylformamide intermediate, only 5.8 mmol/2.45 g cat/hr of
methyldiethylamine would be produced by the direct hydrogenation path
(Eqn. 2)). The remainder would be converted back to the reactants,
diethylamine and methanol. During the methylation of diethylamine
with synthesis gas, 11.2 mmol/2.45 g cat/hr of methyldiethylamine was
produced. Hence, the rate of hydrogenation of N,N-diethylformamide
does not account for the rate of the overall synthesis of methyldi-
ethylamine by synthesis gas and diethylamine. The flow rate depen-
dence study showed that at most, 50% of the methyldiethylamine would
arise by the reaction of diethylamine with surface formate, followed
by the reaction sequence given by Eqns. 9),10). The evidence against
such a participation can be summarized in the following manner. It
has been shown before that surface formate was a common intermediate
for both methanol synthesis and the water gas shift (WGS) reaction
(7). If surface formate underwent amination, one would expect the
rate of the WGS reaction to be lowered as compared with the WGS re-
action rates in the absence of amine but with an equivalent amount of
water. Vedage et al. (7) showed that the WGS reaction rates were un-
affected by the methylation of diethylamine with synthesis gas. There-
fore, the C_1 intermediate undergoing amination is not formate or a
precursor of formate but an intermediate formed subsequent to the sur-
face formate in methanol synthesis. This intermediate can be deduced
as an aldehydic type intermediate by the process of elimination. This
intermediate which can take the form formyl, formaldehyde or hydroxy-
carbene is therefore a kinetically significant intermediate in metha-
nol synthesis.

ACKNOWLEDGMENTS

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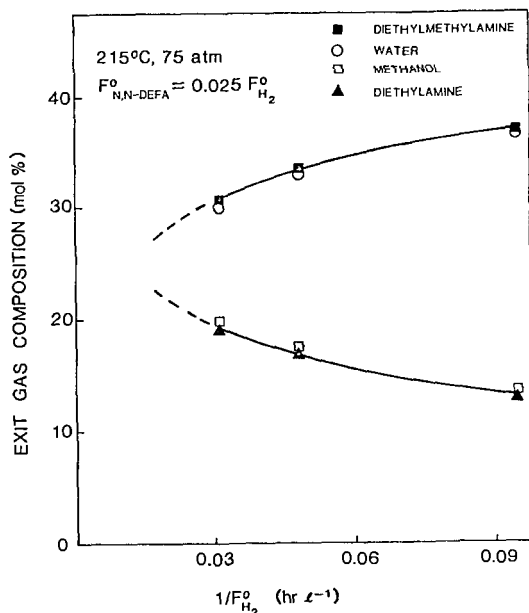(12) J. B. Bulko, R. G. Herman, K. Klier and G. W. Simmons, J. Phys. Chem. 83, 3118 (1979).

Figure 1. Diethylmethylamine, diethylamine, methanol and water produced by Eqns. 2) and 3) as a function of the reciprocal flow rate of hydrogen at 215°C, 75 atm and over 2.45 g Cu/ZnO (30/70) catalyst.